Study on the dielectric properties of Mg-doped $NaBiTi_6O_{14}$ ceramics*

Yong Chen(陈勇)[1], Simin Xue(薛思敏)[1], Qian Luo(骆迁)[1], Huyin Su(苏虎音)[1], Qi Chen(陈琪)[1], Zhen Huang(黄镇)[1], Linfang Xu(徐玲芳)[1], Wanqiang Cao(曹万强)[1,2,†], and Zhaoxiang Huang(黄兆祥)[3,‡]

[1] *School of Physics and Electronic Science, Key Laboratory of Ferro & Piezoelectric Materials and Devices of Hubei Province, Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Wuhan* 430062, *China*

[2] *School of Materials Science and Engineering, Hubei University, Wuhan* 430062, *China*

[3] *Department of Information Science and Technology, WenHua College, Wuhan* 430074, *China*

(Received 18 October 2016; revised manuscript received 20 January 2017; published online 20 February 2017)

With the interest in using lead-free materials to replace lead-containing materials increasing, the use of $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) has come into our sight. We studied the composition of NBT and found that $NaBiTi_6O_{14}$ ceramics can be compositionally tuned by Mg-doping on the Ti-site to optimize the dielectric properties. In this study, Mg-doped $NaBiTi_6O_{14}$ ($NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$) ceramics were prepared by a conventional mixed oxide route at different sintering temperatures, and their dielectric properties have been studied at a wide temperature range. X-ray diffraction (XRD) patterns of the NBT-based ceramics indicate that all samples have a pure phase without any secondary impurity phase. The experimental data show that after Mg-doping, the relative permittivity and dielectric loss become lower at 1040, 1060, and 1080 °C except 1020 °C and at different frequencies from 10 kHz, 100 kHz to 1 MHz. Take 1060 °C for example, when the sintering temperature is 1060 °C at 1 MHz, the minimum relative permittivity of $NaBiTi_6O_{14}$ is 32.9 and the minimum dielectric loss is 0.01417, the relative permittivity of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ under the same condition is 25.8 and the dielectric loss is 0.000104. We explored the mechanism of Mg-doping and surprisingly found that the dielectric property of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ becomes better owing to Mg-doping. Thus, $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ can be used in microwave ceramics and applied to new energy materials.

Keywords: $NaBiTi_6O_{14}$, permittivity, loss $(\tan\delta)$, dielectric ceramics

PACS: 77.22.–d, 77.84.–s **DOI:** 10.1088/1674-1056/26/4/047701

1. Introduction

Ferroelectric materials are particularly significant in the development of modern technology due to their promising dielectric and piezoelectric properties. Piezoelectric materials have been widely used in electronic devices such as sensors, actuators, and transducers.[1–3] In addition, ferroelectric materials are also widely used as dielectric materials in modern electronics applied to bypassing, coupling, filtering, smoothing, and power conditioning.[4] We must point out that we mainly use $Pb(Zr_{1-x}Ti_x)O_3$-based piezoelectric materials nowadays. As the use of lead and other toxic elements has been restricted, the interest in substituting lead-containing materials for lead-free materials has surged recently in order to meet environmental standards such as Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment Directive (WEEE).[5–8] Compared with $BaTiO_3$, PZT and other materials in the perovskite system, NBT has excellent dielectric and piezoelectric properties with higher relative permittivity (ε_r) and lower dielectric loss. NBT exhibits the maximum relative permittivity $\varepsilon_r \sim 3000$ at ~ 320 (T_{max}) and possesses a distorted perovskite structure with extensive chemical, cation-displacement, and octahedral tilt disorder.[9–11] We must emphasize that NBT has a pretty wide operational temperature, so it can be used in many devices and adapt to various temperature conditions. However, NBT can very easily cause Bi leakage. A new Mg-doped $NaBiTi_6O_{14}$ ($NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$) ceramic was prepared through the chemical reaction of Na_2CO_3, Bi_2O_3, MgO, and TiO_2. We studied the composition of $NaBiTi_6O_{14}$ and surprisingly found that $NaBiTi_6O_{14}$ can be compositionally tuned by Mg-doping on the Ti-site to optimize its piezoelectric and dielectric properties. The samples were prepared by the following chemical equation:

$$Na_2CO_3 + 5.88TiO_2 + Bi_2O_3 + 0.12MgO \rightarrow 2NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta} + CO_2\uparrow. \quad (1)$$

This $NaBiTi_6O_{14}$ material with Mg-doping has high relative permittivity and low dielectric loss with a wide operational temperature range. $NaBiTi_6O_{14}$ can be comprehensively used in ceramic capacitors, especially high-temperature capacitors and applied to electronic control systems for hybrid or electrically powered vehicles and microwave ceramics. $NaBiTi_6O_{14}$ also develops a new direction for ceramic capacitors and new energy materials.[12–15]

*Project supported by the Fund from the Hubei Provincial Department of Education, China (Grant No. D20161006).

†Corresponding author. E-mail: caowanq@163.com

‡Corresponding author. E-mail: huangzhaox@163.com

© 2017 Chinese Physical Society and IOP Publishing Ltd

2. Experimental procedure

Reagent grade Na_2CO_3, Bi_2O_3, MgO, and TiO_2 were used as the starting materials of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ (99.9%Na_2CO_3, 99.9%Bi_2O_3, 99.9%TiO_2, 99.9%MgO). These high-purity powders were weighed stoichiometrically and ball-milled with C_2H_5OH for 24 h, then the powders washed and dried in a drying oven were calcined at 950 °C for 2 h. The phase identification was done using a powder x-ray diffractometer (XRD; Bruker D8, Karlsruhe, Germany, Cu Ka∼ 1.5406 A) with Cu Ka radiation; scan speed of 1 °C/min. After being re-milled, the powder was pressed into disks of 10 mm in diameter and 2 mm in thickness. The PVA (polyvinyl alcohol) was heated for 10 h at 650 °C in the air. The compacted disks were sintered at 1020 °C–1100 °C for 9 h in stove (Energy-save-type Quick temp raising Electric furnace), then cooled down to room temperature. The sintered disks were polished and examined by x-ray diffraction on a Philips X'Pert diffractometer again. Finally, the dishes were covered with silver paste and the electrode of the dishes was baked. After the preparation of $NaBiTi_6O_{14}$, high-temperature IS measurements were performed using an impedance analyzer (Agilent 4194 A, Agilent) in a non-inductively wound tube furnace. The relative permittivity and dielectric loss were tested by an impedance analyzer (HP Agilent, 4192 A Hewlett Packed, Santa Clara, CA) between 100 °C and 700 °C. The microstructure of $NaBiTi_6O_{14}$ was observed by scanning electron microscope (SEM JEOL Ltd., Tokyo, Japan).

3. Results and discussion

3.1. XRD results

The XRD patterns of sintered pellets of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ are displayed in Fig. 1. The x-ray diffraction patterns of the NBT-based ceramics indicate that all samples have a pure phase. Figures 1(a) and 1(b) show the XRD patterns of well-sintered $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramic disks respectively. The XRD results show a major phase of $NaBiTi_6O_{14}$ solid solution. It can be seen that all samples maintain the tetragonal perovskite structure. According to the XRD spectrum analysis, the peak shifted to the right after Mg-doping, which indicated that interplanar spacing became larger which was mainly attributed to the substitution of relatively larger Mg^{2+} into Ti sites. Based on Bragg's Law, $2d\sin\theta = n\lambda$, under the condition that the wavelength of incident light remains unchanged. What has been mentioned above elaborates the reason why the peak appears later in the XRD spectrum. This could be understood by the oxygen vacancy compensation mechanism:

$$MgO + Ti_{Ti} + O_o \rightarrow Mg'_{Ti} + TiO_2 + V_{\ddot{O}}. \quad (2)$$

When the samples were sintered at a temperature from 1020 °C to 1080 °C, the substitution of Mg^{2+} into Ti sites which follows oxygen vacancy compensation mechanism explains the formation of TiO_2. It has been reported that substituting Ti ions for larger ions in the oxygen octahedral could modify the polarization of NBT-based materials effectively. In this case, when larger Mg^{2+} occupied Ti sites, the Mg^{2+} was centrally located in the oxygen octahedral and got "stuck". Since the polarization of the system mainly originated from the Ti^{4+} deviating from the central region of the octahedra, relatively larger Mg^{2+} prevented the deviation and thus produced changes in the polarization, besides, the larger Mg^{2+} inflated the octahedra which probably altered the adjacent octahedra and thus inhibited the formation of ferroelectric domains. As a result, the tetragonality decreased and the formation of the ferroelectric domains was suppressed. What should be mentioned here is why there is no TiO_2 phase. TiO_2 content is too low so that it cannot be detected by XRD. In addition, TiO_2 may be involved in the reaction in Eq. (2). Therefore, the existence of TiO_2 will not affect XRD results.

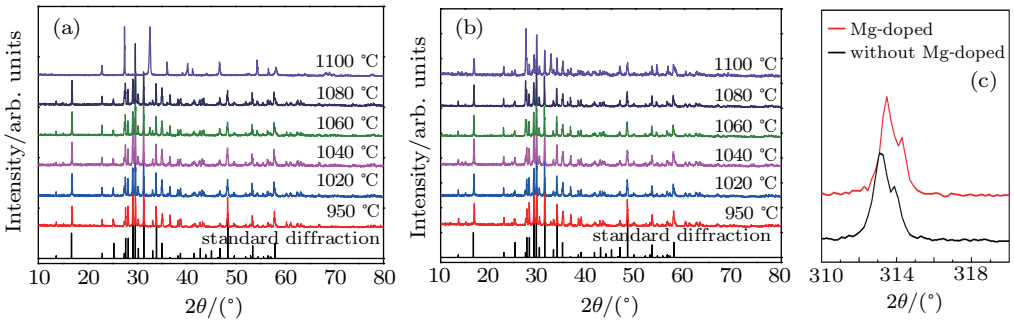


Fig. 1. (color online) X-ray diffraction patterns of calcined and sintered $NaBiTi_6O_{14}$ (a) and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ powders (b).

3.2. Relative permittivity

Impedance spectroscopy measures the dielectric properties of ceramic samples as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, usually expressed by permittivity. The frequency dependence of relative permittivity (ε_r) of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics sintered at 1020, 1040, 1060, and 1080 °C are shown

in Fig. 2. By processing the experimental data, we can find that the relative permittivity of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14}$ is a little lower than that of $NaBiTi_6O_{14}$. Figure 3 shows the temperature dependence of relative permittivity of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics at 1 MHz. Despite 1020 °C, the relative permittivity of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is lower than that of $NaBiTi_6O_{14}$. The relative permittivity drops pretty fast at first, and then keeps stable, and finally increases quickly. We can describe the general trend of permittivity as a 'U' shape. At different frequencies, the general trend remains the same. Relative permittivity decreases with the increase of frequency. At different sintering temperatures, the general trend still remains a 'U' shape. Relative permittivity decreases with the increase of sintering temperature. When the sintering temperature is 1040 °C at 1 MHz, the relative permittivity is 27.2. With respect to ion radius, the radius of Mg^{2+} is 0.072 nm, the radius of Ti^{4+} in the B site is 0.064 nm. The radius of Mg^{2+} is similar to that of Ti^{4+}, so it is possible to occupy Ti^{4+}'s position. When Mg^{2+} occupies the B site of Ti^{4+}, oxygen vacancies will appear. The deformation of the perovskite structure makes it difficult for the domain to move. When oxygen vacancies diffuse to the domain wall, they will nail the domain easily and block the movement of the domain which makes it difficult for the domain to change direction. Therefore, piezoelectric and dielectric properties of ceramics will decrease.[16]

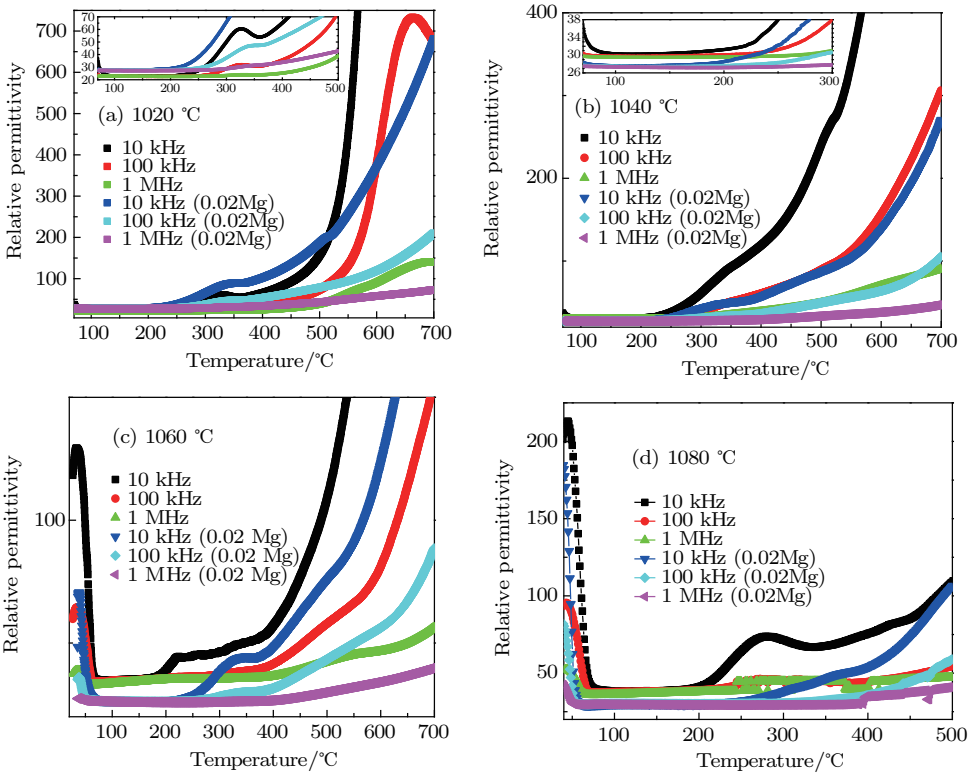


Fig. 2. (color online) Relative permittivity of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics sintered at (a) 1020 °C, (b) 1040 °C, (c) 1060 °C, and (d) 1080 °C.

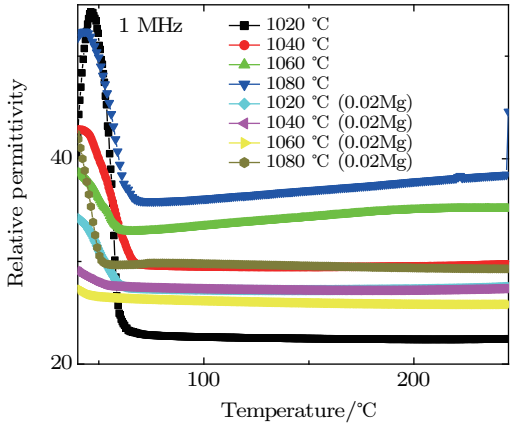


Fig. 3. (color online) The relative permittivity of $NaBiTi_6O_{14}$ and $NaBi(Ti_{5.98}Mg_{0.02})_6O_{14-\delta}$ ceramics at 1 MHz at different temperatures.

3.3. Dielectric loss

The dielectric loss of the samples sintered at 1020, 1040, 1060, and 1080 °C is shown in Fig. 4. Figure 4 shows the frequency dependence of the dielectric loss tangent $(\tan\delta)$ of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ at different temperatures. In all sintering temperatures, the general trend is that $\tan\delta$ of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is lower than that of $NaBiTi_6O_{14}$. For example, when the sintering temperature is 1040 °C at 1 MHz, the minimum dielectric loss of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is 0.00248. The minimum dielectric loss of $NaBiTi_6O_{14}$ under the same condition is 0.100. It is very obvious that after Mg-doping, the dielectric loss becomes lower. Figure 4 also shows that the dielectric loss remains a very low level from around 100 °C to 600 °C, which implies

that $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ can be comprehensively used in a ceramic capacitor, microwave ceramics with a pretty wide operational temperature. Similar to the change trend of the relative permittivity, the dielectric loss drops very fast at first, then keeps stable, and finally increases quickly. We can describe the general trend of dielectric loss as a 'U' shape. At different frequencies, the general trend remains the same. Dielectric loss decreases with the increase of frequency. At different sintering temperatures, the general trend still remains a 'U' shape. Dielectric loss decreases with the increase of sintering temperature. Figure 5 shows the temperature dependence of the dielectric loss tangent ($\tan\delta$) of the $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ at 1 MHz. As the temperature increases, the dielectric loss keeps on decreasing until the temperature reaches 1060 °C, and then increases a little between 1060 °C and 1080 °C. There is a theory that may explain the reason why the dielectric loss increases between 1060 °C and 1080 °C. The interface polarization between the grain and grain boundary is weak. With the increase of temperature, the resistivity of the ceramics decreases and the conductivity of the grains becomes obvious, namely that the interaction between ceramics and electrodes begins to influence ceramic properties.[17] Consequently, at high temperatures, the dielectric loss increases with the increasing temperature. Generally, the dielectric loss of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is about one order of magnitude lower than $NaBiTi_6O_{14}$ at the same sintering temperature, which indicates that the dielectric property of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is better than that of $NaBiTi_6O_{14}$. The reason why the dielectric loss becomes lower after Mg-doping in $NaBiTi_6O_{14}$ might be attributed to the decrease of the grain size. Large grain size causes the decrease of the ratio of the grain boundary. Generally, the defects in the grain boundary are less than that in grain, leading to the decrease of the dielectric loss.[18–20]

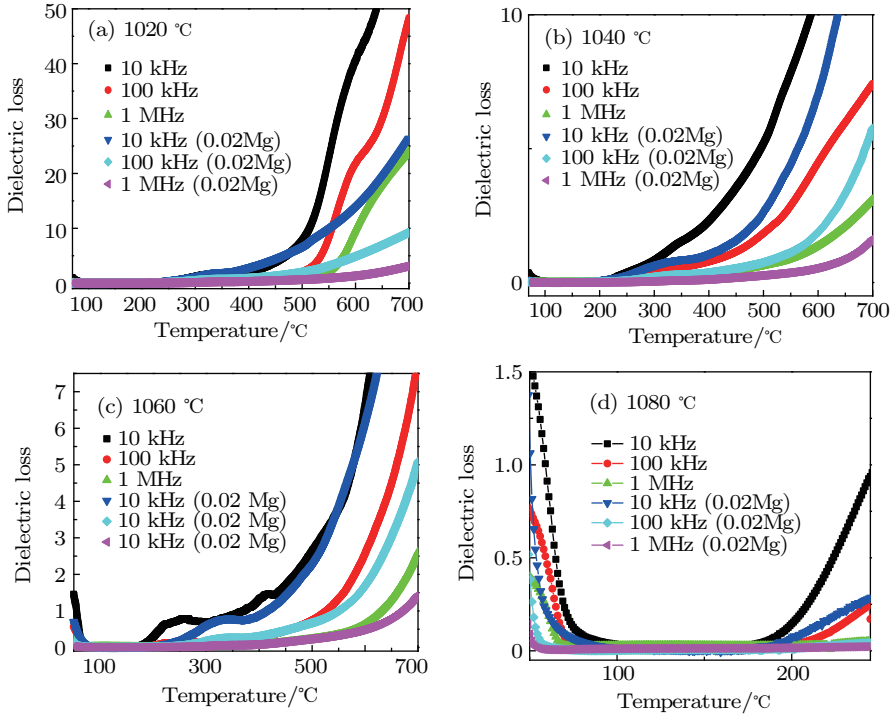


Fig. 4. (color online) The dielectric loss of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics sintered at (a) 1020 °C, (b) 1040 °C, (c) 1060 °C, and (d) 1080 °C.

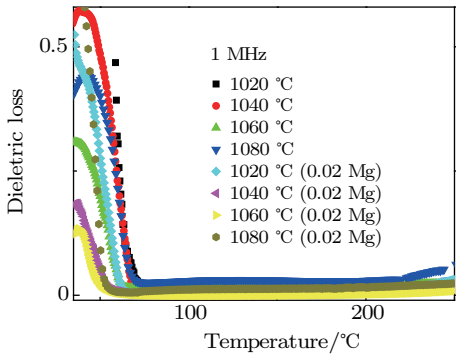


Fig. 5. (color online) The dielectric loss of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics at 1 MHz at different temperatures.

3.4. Dielectric properties

The bulk densities of disks were measured as a function of the sintering temperature and the results are listed in Table 1. It is obviously seen in Table 1 that the bulk density of undoped samples ($NaBiTi_6O_{14}$) increases with the sintering temperature increasing. However, after Mg-doping, the bulk density of samples is always maintained at about 3.6 g/cm^3 which is not very different from the undoped samples. As a result, it is concluded that densification of the system can be improved by higher sintering temperatures. We can also see from Table 1 that insulation resistance of all samples is roughly maintained

at six party orders of magnitude. High insulation resistance demonstrates all the samples are dielectrics. Table 2 shows the dielectric properties (the minimum relative and permittivity dielectric loss) of the samples sintered at 1020, 1040, 1060, and 1080 °C at 1 MHz. In general, with the increasing sintering temperature, the relative permittivity of all samples is between 22 and 36, and there is not much difference. The relative permittivity and the dielectric loss of $NaBiTi_6O_{14}$ increase gradually with the sintering temperature increasing. The relative permittivity of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ does not vary much with the change of sintering temperature. It is demonstrated once again that the relative permittivity and the dielectric loss of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ are lower than that of $NaBiTi_6O_{14}$ at the same sintering temperature except 1020 °C, indicating that $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics have excellent dielectric property. These intriguing properties make this material qualify for practical applications.

The scanning electron microscope (SEM) micrographs of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ sintered at different temperatures are shown in Fig. 6 and Fig. 7, respectively. To a certain degree, the dielectric constant can reflect the function of materials. Comparing the two pictures, we can observe that in general, the grain size of Mg-doped samples is slightly smaller than that of $NaBiTi_6O_{14}$ ceramics. More specifically, the grain shown in Fig. 6 is more homogeneous. The domain reorientation of the ceramics becomes more difficult and restricts the movement of the domain wall due to the strong coupling between the grain boundaries and the domain wall. Then the value of remnant polarization decreases, and the relative permittivity also increases accordingly. In the end, we can draw a conclusion that the relative permittivity and the dielectric loss of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is smaller than that of $NaBiTi_6O_{14}$ at the same condition, which is consistent with Table 2.

Table 1. Dielectric properties of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ samples sintered at different temperatures.

Sample	Temperature/°C	Bulk density/(g/cm^3)		Insulation resistance (ρ_v)/10^6 Ω·cm	
		$NaBiTi_6O_{14}$	$NaBi(Ti_{0.98}Mg_{0.02})_6O_{14}$	$NaBiTi_6O_{14}$	$NaBi(Ti_{0.98}Mg_{0.02})_6O_{14}$
1	1020	3.173	3.774	0.0481	0.0975
2	1040	3.895	3.643	41.7895	0.4365
3	1060	4.057	3.587	4.0662	3.9322
4	1080	4.099	3.511	4.2834	3.9051

Table 2. Dielectric properties of $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ samples sintered at different temperatures.

Sample	Temperature/°C	ε_r		tan δ/%	
		$NaBiTi_6O_{14}$	$NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$	$NaBiTi_6O_{14}$	$NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$
1	1020	22.3962	27.2043	0.050	0.151
2	1040	29.4388	27.1733	0.248	0.101
3	1060	32.9143	25.8045	1.417	0.100
4	1080	35.8533	29.2735	2.509	0.112

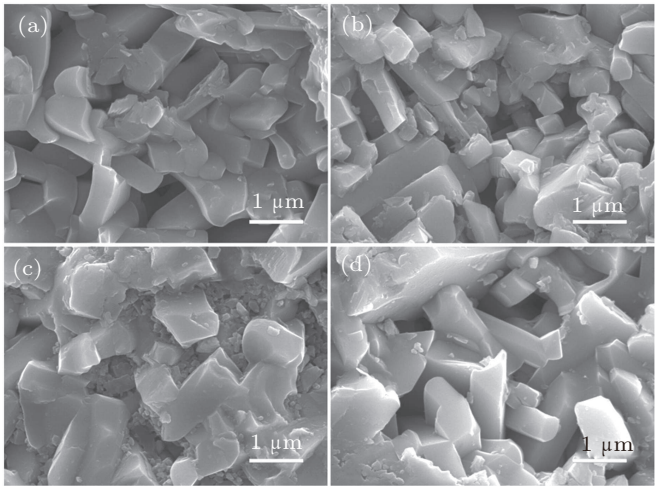


Fig. 6. SEM of $NaBiTi_6O_{14}$ ceramics sintered at (a) 1020 °C, (b) 1040 °C, (c) 1060 °C, and (d) 1080 °C.

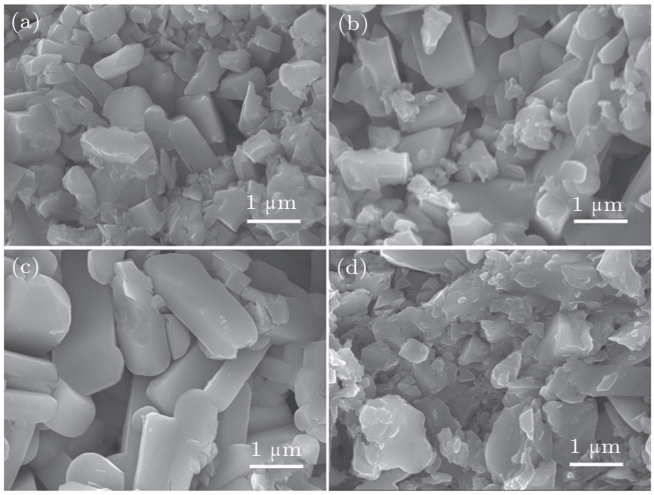


Fig. 7. SEM of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ ceramics sintered at (a) 1020 °C, (b) 1040 °C, (c) 1060 °C, and (d) 1080 °C.

4. Conclusion

In this article, we studied the dielectric property by comparing $NaBiTi_6O_{14}$ and $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$, we mainly focused on the relative permittivity and the dielectric loss of the samples and found that the dielectric property of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is better than that of $NaBiTi_6O_{14}$.

(i) According to the above discussion, we find that despite 1020 °C, the relative permittivity (ε_r) of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is lower than that of $NaBiTi_6O_{14}$ at the same sintering temperature. In addition, the dielectric loss remains at a very low level around 100 °C to 600 °C, indicating that the dielectric property of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ is better than that of $NaBiTi_6O_{14}$. The dielectric property of $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ implies that $NaBi(Ti_{0.98}Mg_{0.02})_6O_{14-\delta}$ can be comprehensively used in microwave ceramics with a pretty wide operating temperature.

(ii) The change of the permittivity after Mg-doping is mainly contributed to the oxygen vacancies. When Mg^{2+} occupies the B site of Ti^{4+}, oxygen vacancies will appear. The deformation of the perovskite structure octahedron makes domain moving difficult. When oxygen vacancies diffuse to the domain wall, they will nail the domain easily and block the movement of the domain which makes it difficult for the domain to change direction in poling. Therefore, piezoelectric and dielectric properties of ceramics will decrease.

(iii) The change of the dielectric loss after Mg-doping is mainly attributed to the interface polarization and the grain size. The interface polarization between the grain and the grain boundary is weak. With temperature rising, the resistivity of the ceramics decreases and the conductivity of grains becomes obvious, namely that the interaction between ceramics and electrodes begins to influence ceramic properties. Consequently, at high temperatures, the dielectric loss increases with the increasing temperature. As for grain size, large grain size causes the decrease of the ratio of the grain boundary. Generally, the defects in the grain boundary are less than that in the grain, leading to the decrease of the dielectric loss.

Acknowledgment

Yong Chen wishes to thank China Scholarship Council (CSC). CSC supports him as an academic visitor to join Derek C Sinclair's research group at the Department of Materials Science and Engineering, University of Sheffield. Yong Chen also gratefully acknowledges the funding provided by the National Natural Science Foundation of China (Grant No. 51202063). Thanks are expressed to Dr. Linhao Li at the University of Sheffield for his helpful discussion and suggestion on impedance spectroscopy. The authors are grateful to Andrew Mould and Nik Reeves-McLaren for advice with electrical measurement.

References

[1] Cao W Q, Liu P Z, Chen Y, *et al*. 2016 *Acta Phys. Sin.* **65** 137701 (in Chinese)
[2] Chen Y, Gong S, Zhang B, *et al*. 2013 *Microelectron. Eng.* **103** 106
[3] Huang H H, Chen Y, Li Z, *et al*. 2015 *J. Wuhan University of Tech. -Mater. Sci. Edn.* **30** 674
[4] Cao W Q and Shang X Z 2015 *Ferroelectr. Lett.* **42** 132
[5] Chen Y, Zhang S, Li Z, *et al*. 2016 *J. Wuhan University of Tech. -Mater. Sci. Ed.* **31** 87
[6] Chen Y, Gong S P, Fu Q Y, *et al*. 2010 *Chin. Phys. B* **19** 117301
[7] Hansen P, Hennings D and Schreinemacher H 1998 *J. Am. Ceram. Soc.* **81** 1369
[8] Kishi H, Kohzu N, Iguchi Y, Sugino J and Kato M 2001 *J. Eur. Ceram. Soc.* **21** 1643
[9] Nam S P, Lee S G, Bae S G and Lee Y H 2007 *J. Electrical Eng. Technol.* **2** 98
[10] Zang J, Li M, Sinclair D C, J Wook and R Jürgen 2014 *J. Am. Ceram. Soc.* **97** 1523
[11] Li M, Pietrowski M J, De Souza R A, Zhang H, Reaney I M, Cook S N, Kilner J A and Sinclair D C 2014 *Nat. Mater.* **13** 31
[12] Huang X, Gao C, Wei M, Z Chen and Y Cui 2011 *Rare Met.* **30** 72
[13] Guo Y, Xiao P, Luo L, *et al*. 2014 *J. Mater. Sci.: Mater. Electron.* **25** 3753
[14] Zang J, Li M, D.C. Sinclair, W. Jo and J. Rödel 2014 *J. Am. Ceram. Soc.* **97** 1523
[15] Li M, Feteira A, Mirsaneh M, Lee S, Lanagan M T, Randall C A and Sinclair D C 2010 *J. Am. Ceram. Soc.* **93** 4087
[16] Li Z F, Chan W, Li Y X, Kwok K W and Choy S H 2010 *J. Alloys Compd.* **41** 70
[17] Feng C, Yang C H, Geng F J, Lv P P and Yao Q 2015 *J. Eur. Ceram. Soc.* **36**
[18] Lei W, Yan Y Y, Wang X H, Lu W, Yang Z B and Lu W Z 2015 *Ceram. Int.* **41** 521
[19] Li M, Feteira A, Mirsaneh M, Lee S, Lanagan M T, Randall C A and Sinclair D C 2010 *J. Am. Ceram. Soc.* **93** 4087
[20] Chen Y, Bian M Y, Zhang C C, Chen Q, Luo Q, Huang Z, Cao W Q, Pan R K and Qi Y J 2017 *Sci. China Ser. E* **47** 32 (in Chinese)